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(54) **Method for producing nuclear fuel pellets of the mox type**

(57) This invention refers to a method for producing nuclear fuel pellets of the MOX (mixed plutonium and uranium oxide) type, comprising the steps of

- preparing an U-Pu oxide blend powder having a Pu content in excess of the finally desired value,
- preparing an uranium oxide powder,
- mixing adequate quantities of both powders in order to achieve the desired plutonium content,
- compacting and sintering the mixture for obtaining said pellets.

According to the invention the step of preparing the uranium oxide powder involves the following sequence

of substeps:

- a) preparation of an aqueous solution of uranyl nitrate to which between 0.5 and 2 wt% of organic thickeners are added such that the viscosity of the solution is adjusted to values between 20 and 100 centipoise,
- b) dispersion of the solution into droplets,
- c) introducing said droplets into a hydroxide bath,
- d) washing the resulting beads,
- e) drying the beads by azeotropic distillation using an immiscible organic solvent,
- f) thermal treatment of the beads in an oxidising atmosphere,
- g) thermal treatment in a reducing atmosphere.

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## Description

[0001] This invention refers to a method for producing nuclear fuel pellets of the MOX (= mixed oxide) type, comprising the steps of

- preparing an U-Pu oxide blend powder having a Pu content in excess of the finally desired value,
- preparing an uranium oxide powder,
- mixing adequate quantities of both powders in order to achieve the desired plutonium content,
- compacting and sintering the mixture for obtaining said pellets.

[0002] Such a method is known under the term MIMAS ("Micronized MASTER Blend" - see for example D. Haas, M. Lippens "MOX FUEL FABRICATION AND IN-REACTOR PERFORMANCE", Proc. of the Internat. Conference on Future Nuclear Systems, GLOBAL 97, p.489 à 494). This separate preparation of a powder free of plutonium reduces the volume of plutonium-containing powder that has to be milled, and allows the production of fuel pellets of various plutonium contents with a unique plutonium treatment chain by changing only the rate of admixed uranium powder.

[0003] The commercial powders currently used, however, result in a final product which is heterogeneous, i. e. contains large particles rich in plutonium oxide dispersed within an uranium oxide matrix whose grain size is below 10  $\mu\text{m}$ . This heterogeneity leads to two major drawbacks:

[0004] During irradiation localised higher fissile material concentrations lead to high local burnups, to fission damages and to gas release. To limit this gas release large  $\text{UO}_2$  grains are recommended, provided that they are produced without additives that might lead to detrimental fuel behaviour during irradiation and might also lead to difficulties during reprocessing.

[0005] During reprocessing the dissolution of the burned-up fuel in nitric acid is hindered by regions rich in plutonium, which is notoriously insoluble.

[0006] The present invention aims to overcome these drawbacks and to propose a method as indicated above which leads to fuel pellets of the MOX type in which the distribution of plutonium throughout the pellet is substantially more homogeneous.

[0007] This aim is achieved by the method as defined in claim 1. As far as preferred embodiments of this method are concerned, reference is made to the secondary claims.

[0008] The invention will now be described in detail by means of preferred embodiments.

[0009] In agreement with the known MIMAS method as cited above, the method according to the invention implies the separate preparation of a Pu-U oxide powder on the one hand and an uranium oxide powder free of plutonium on the other hand.

[0010] According to a first embodiment the Pu-U oxide

powder is prepared conventionally by mechanically milling  $\text{PuO}_2$  and  $\text{UO}_2$  materials, whereas the  $\text{UO}_2$  powder is prepared as follows:

[0011] To an aqueous solution of uranyl nitrate small amounts, i.e. between 0.5 and 2 wt%, of organic thickeners are added, such as methocel, dextran, polyvinyl alcohol, such that the viscosity of the solution is adjusted to values between 20 and 100 centipoise. Thereafter, this solution is dispersed into droplets, which are introduced into an ammonia bath. In this bath, due to the network formed by the long chain organic polymers, precipitation occurs within the original droplets, so that nearly spherical beads are formed. The size of these beads depends on the size of the droplets produced during dispersion. In a preferred embodiment these beads present diameters of between 20 and 50  $\mu\text{m}$ . These beads are then washed to remove nitrate salts (ammonium nitrate salts in the above example) and organic polymers, and are subjected to an azeotropic distillation using an immiscible organic solvent such as  $\text{C}_2\text{Cl}_4$  to remove water.

[0012] Once dried the beads are in a hydroxide form, from which they are converted to oxide by a thermal treatment of between 2 and 6 hours duration and at about 400°C in air. Thereby residual organic polymers are pyrolysed. The beads are then again submitted to a thermal treatment of between 4 and 8 hours duration, this time at about 800°C and in a reducing atmosphere of Ar/5% $\text{H}_2$ , to convert  $\text{U}_3\text{O}_8$  to  $\text{UO}_2$ .

[0013] The beads can be produced by conventional uranium processing facilities (no  $\alpha$  contamination). They are free flowing, dust free and do not require any further mechanical treatment such as milling prior to mixing with the powder containing plutonium. The homogeneity of the finally produced fuel can further be enhanced by sieving the beads and retaining only beads with diameters in the range of 20 to 50  $\mu\text{m}$ . Alternatively this result can also be achieved by using a droplet dispersion device which produces droplets of well defined size such that the bead diameters remain within said range and no sieving becomes necessary.

[0014] Once mixed the MOX powder is compacted into pellets by using a press which applies a pressure of between 200 and 600 MPa. These pellets are then sintered at high temperature, preferably at 1700°C, in a humidified Ar/ $\text{H}_2$  atmosphere, the hydrogen content of which lies between 1 and 6% and the water vapour introduction should result in a ratio of the partial  $\text{H}_2$  pressure to the water vapour partial pressure of between 20 and 60. The water allows to control the oxygen potential of the gas atmosphere which results in an enhanced diffusion and in a more homogeneous fuel thus enabling a longer burn-up in the reactor.

[0015] According to a variant of the method the powder containing an excess content of plutonium can be prepared in the same way as above described for the uranium oxide powder, but by starting with uranyl-plutonium nitrate instead of uranyl nitrate.

[0016] The inventive method can be realised in conventional MOX fabrication facilities and conserves all the advantages of the MIMAS process but does not suffer from the drawbacks of this process as mentioned above.

#### Claims

1. A method for producing nuclear fuel pellets of the MOX (mixed plutonium and uranium oxide) type, comprising the steps of

- preparing an U-Pu oxide blend powder having a Pu content in excess of the finally desired value,
- preparing an uranium oxide powder,
- mixing adequate quantities of both powders in order to achieve the desired plutonium content,
- compacting and sintering the mixture for obtaining said pellets,

characterized in that the step of preparing the uranium oxide powder involves the following sequence of substeps:

- a) preparation of an aqueous solution of uranyl nitrate to which between 0.5 and 2 wt% of organic thickeners are added such that the viscosity of the solution is adjusted to values between 20 and 100 centipoise,
- b) dispersion of the solution into droplets,
- c) introducing said droplets into a hydroxide bath,
- d) washing the resulting beads,
- e) drying the beads by azeotropic distillation using an immiscible organic solvent,
- f) thermal treatment of the beads in an oxidising atmosphere,
- g) thermal treatment in a reducing atmosphere.

2. A method according to claim 1, characterized in that the step of preparing an U-Pu oxide blend powder consists in milling and mixing adequate quantities of uranium oxide and plutonium oxide.

3. A method according to claim 1, characterized in that the step of preparing the U-Pu oxide blend powder involves the following sequence of substeps:

- a) preparation of an aqueous solution of uranyl-plutonium nitrate to which small amounts of organic thickeners are added in order to adjust the viscosity of the solution to values between 20 and 100 centipoise,
- b) dispersion of the solution into droplets,
- c) introducing said droplets into a hydroxide bath,

- d) washing the resulting beads,
- e) subjecting the beads to an azeotropic distillation using an immiscible organic solvent,
- f) thermal treatment of the beads in an oxidising atmosphere,
- g) thermal treatment in a reducing atmosphere.

4. A method according to anyone of the preceding claims, characterized in that in substep a) the organic thickeners are selected among methocel, dextran and polyvinyl alcohol.

5. A method according to anyone of the preceding claims, characterized in that in substep c) the hydroxide bath consists of ammonia.

6. A method according to anyone of the preceding claims, characterized in that in substep f) the thermal treatment in an oxidising atmosphere is performed at about 400°C and in air.

7. A method according to anyone of the preceding claims, characterized in that in substep g) the thermal treatment in a reducing atmosphere is performed at about 800°C, the reducing atmosphere containing an inert gas with a hydrogen content between 1 and 6%.

8. A method according to anyone of the preceding claims, characterized in that compacting of the powder mixture into pellets is obtained by applying a pressure of between 200 and 600 MPa.

9. A method according to anyone of the preceding claims, characterized in that the sintering of the pellets takes place at a temperature above 1200°C, preferably between 1600 and 1700°C, and in a humidified Ar/H<sub>2</sub> atmosphere, the hydrogen content lying between 1% and 6% and the ratio between the partial pressures of hydrogen and water vapour being selected between 20 and 60.

10. A method according to anyone of the preceding claims, characterized in that before mixing adequate quantities of both powders, the UO<sub>2</sub>-powder is sieved in order to retain only beads with diameters between 20 and 50µm size.



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## EUROPEAN SEARCH REPORT

Application Number  
EP 99 11 6886

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 498 138 A (INST NUCLEAR ENERGY RES) 12 August 1992 (1992-08-12) * claims 1,2,5,7,12,16 *	1,3,5-7	G21C21/02
A	DD 33 300 A (SCHEIBE) 5 December 1964 (1964-12-05) * the whole document *	1,3,5	
A	FR 1 567 033 A (NUKEM) 16 May 1969 (1969-05-16) * résumé *	1,3,5-7	
A	FR 2 582 641 A (MITSUBISHI METAL CORP) 5 December 1986 (1986-12-05) * claims 1,2 *	1,3,5	
A	WO 87 00543 A (VAMP SRL) 29 January 1987 (1987-01-29) * claims 1-9 *	1,3-7	
A	EP 0 322 481 A (MITSUBISHI METAL CORP) 5 July 1989 (1989-07-05) * claims 1-6 *	1,3,5-7	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
D,A	D. HAAS; M. LIPPENS: "MOX FUEL FABRICATION AND IN-REACTOR PERFORMANCE" GLOBAL 97, pages 489-494, XP002128560 * the whole document *	1-10	G21C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 January 2000	Examiner Deroubaix, P
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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24-01-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0498138 A	12-08-1992	DE 69119577 D	20-06-1996
		DE 69119577 T	05-12-1996
		US 5139709 A	18-08-1992
DD 33300 A		NONE	
FR 1567033 A	16-05-1969	BE 702075 A	02-01-1968
		DE 1592478 A	23-12-1970
		GB 1206048 A	23-09-1970
		SE 328559 B	21-09-1970
		US 3519403 A	07-07-1970
FR 2582641 A	05-12-1986	JP 1654575 C	13-04-1992
		JP 3013172 B	21-02-1991
		JP 61281019 A	11-12-1986
		CN 1007344 B	28-03-1990
		DE 3618695 A	04-12-1986
		GB 2177386 A,B	21-01-1987
		KR 8904802 B	27-11-1989
WO 8700543 A	29-01-1987	US 4808390 A	28-02-1989
		IT 1187702 B	23-12-1987
EP 0322481 A	05-07-1989	EP 0230439 A	05-08-1987
		CN 1033785 A,B	12-07-1989
		US 4963294 A	16-10-1990

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82